Metal Remediation using Polymeric Hydrogel - A Green Adsorbent

Synopsis

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in

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Submitted by

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1. Introduction

1.1 Adsorption as a Method of Metal Recovery

Metals, in addition to being finite and nonrenewable resources, are crucial to developmental needs of human population. Extraction of metals from ores by mining is unsustainable and hazardous (Rebello et al. 2021). Mining affects human population in several ways; drinking water contamination, bio-accumulation in food crops and damage of natural landscape being the most detrimental aspects of mining related hazards (Khalilova and Mammadov 2016; Lei et al. 2016). For above mentioned reasons, need for metal extraction and recovery from industrial effluent, e-waste and other secondary sources (metal scrap etc.) becomes imperative.

Prominent methods for metal extraction and recovery are adsorption, ion exchange, precipitation, coagulation, membrane filtration, liquid-liquid extraction, electrochemical removal etc. (Li et al. 2019; Shyam Sunder et al. 2020). Adsorption process is economic, efficient, selective and has low energy requirement along with ease of operation (Chen et al. 2011).

1.2 Common Industrial Adsorbents and Greener Alternatives

Conventional industrial adsorbents are derivatives of activated carbon, graphene, carbon nanotubes, zeolites etc. These industrial adsorbents generally include some significant drawbacks such as energy intensive production (e.g., pyrolysis), tricky disposal-regeneration and overall high process cost (Crini et al. 2018). Some of the less common or unconventional adsorbents are clay minerals, farm waste-based adsorbents, sludge-based adsorbents, biochar etc. (Khalil et al. 2020). Hydrogels are relatively new products in the developments of alternative adsorbents, which are three-dimensional network synthesized by cross linking of polymers using excess amount of water as solvent. Hydrogels are emerging as alternative green adsorbents because they are highly porous, hydrophilic, non-toxic and have high functionality (Duman et al. 2020). Some examples of polymers used in synthesis of hydrogel-based adsorbents are cellulose, polyacrylic acid, gelatin, chitosan, polyvinyl alcohol, thiourea etc. (Perumal et al. 2021).

1.3 Hydrogels: Properties, Applications and Synthesis

Cellulose is the most abundant chemical resource on earth (Sharma et al. 2019), and the hydroxyl groups on cellulose provide feasibility for synthesis of multiple structures of hydrogels. Cellulose

hydrogels are valuable resource which have registered applications in field of biomaterials, agriculture, medicine, water purification, adsorption etc. (Chang and Zhang 2011). Biomaterials fabricated from cellulose hydrogel have recently found application in wound dressing, drug delivery (Kumar et al. 2017), tissue engineering (Phan et al. 2021) etc. This study focuses on the recovery of metals from waste streams using selective adsorption properties of hydrogel.

The abundance of hydroxyl groups in cellulose structure is the key to synthesis of cellulose hydrogels. Physical and chemical cross linking are the main routes of synthesis (Ma et al. 2015). Some of the less common synthesis methods are viscosity adjustment and microwave irradiation (Giachi et al. 2011), or a combination of above-mentioned methods. Some examples of the hydrogel derivatives synthesized using chemical cross linking are- Carboxy Methyl Cellulose (CMC), Carboxy Methyl Cellulose Epichlorohydrin (CMC-ECH), Cellulose acetate, Cellulose nitrate, Carboxymethyl-diethylammoniumethyl Cellulose (CMDEAEC) etc.

1.4 Theoretical Studies of Adsorption using Density Functional Theory

In reference to theoretical study of adsorption of metals, Density Functional Theory (DFT) is a useful tool to understand different parameters of adsorption such as binding energy, Frontier Molecular Orbital analysis, preferential adsorption sites, and the interaction between two functional groups (Reis et al. 2019).

Density functional theory is a prominent quantum mechanical simulation method which uses the principle that properties of multiple electron systems can be determined using functional (function of a function) of their electron density values. The probable structure, spectra and free energy can be calculated and then in the experimental stage of study these can be compared with laboratory results.

1.5 Metal Recovery by Adsorption on Hydrogel

Desired characteristics of an adsorbent applicable for metal recovery are following- ease of regeneration, economy of process, selectivity, eco-friendly end of life disposal, high adsorption affinity etc. (Mondal 2019). Porous structure of hydrogels implies high surface area per unit weight of hydrogel, this along with abundant functional groups results in high adsorption affinity. Additionally, cellulose-based hydrogels are nontoxic, bio-compatible and bio-degradable (Fu and Wang 2011; Ma et al. 2015).

By modifying the surface functional group to target a specific metal ion, selectivity of hydrogel can be increased (Badsha et al. 2021). For instance, recovery of monovalent Lithium (from spent Lithium-ion battery) and recovery of divalent Nickel (from industry effluent) would require different functional group modified hydrogels (Alexandratos 2018). The selectivity of adsorption, beyond the surface functional group, is also understood to depend on the electronegativity and ionic radius of metal ion (covalent index) (Zhu et al. 2012). In brief, hydrogel checks most of the boxes for an efficient adsorbent for metal recovery by adsorption.

To summarize the major points of this chapter, **fig 1** represents a schematic of the following-

- Pretreatment of lignocellulosic biomass (rice straw) for its separation into individual components,
- Synthesis of cellulose hydrogel and
- Mechanism of metal adsorption using cellulose hydrogel.

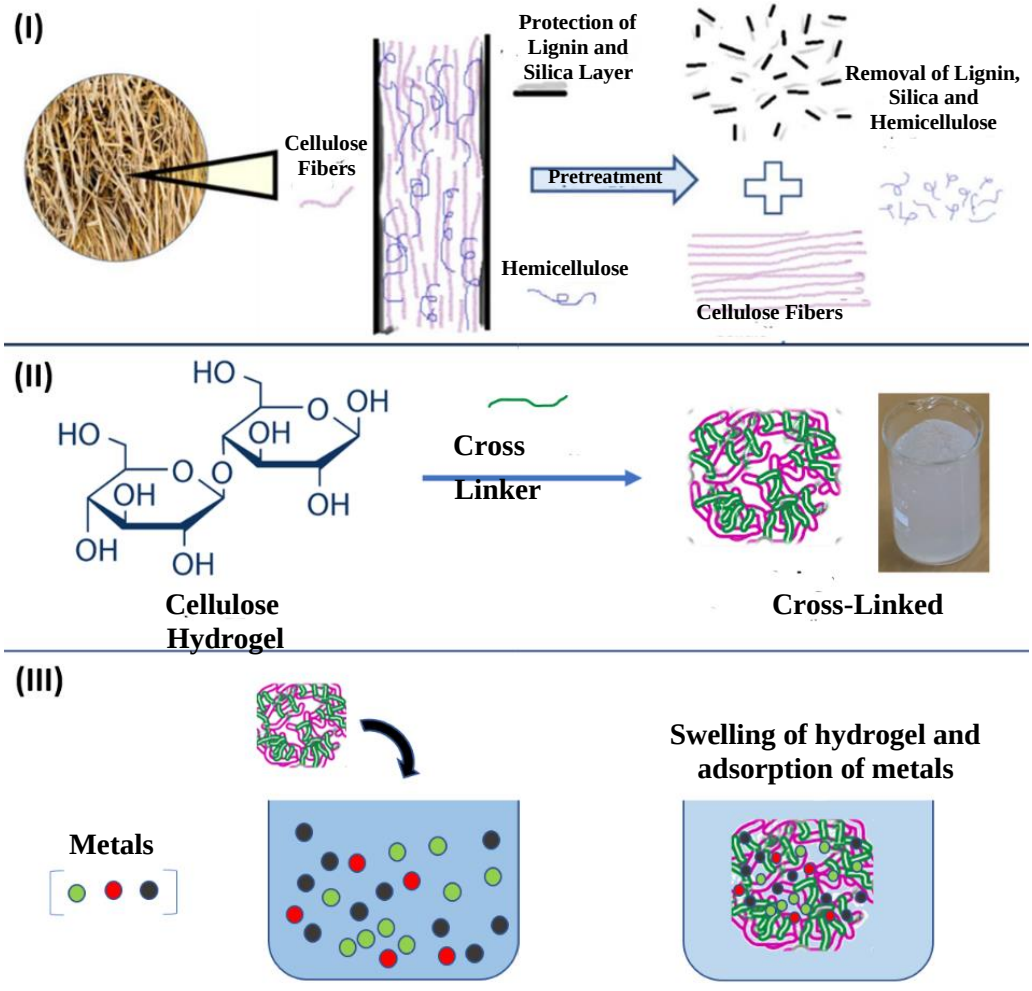

Figure 1. Schematic of hydrogel formation and adsorption of metals

2. Objectives of Study

2.1 To Design a Novel Process for Metal Recovery from Waste

Primary aim of the study is recovery of metals from metal bearing wastes (e.g., e-waste, catalytical waste, metallurgical process waste) via adsorption. This will be achieved by theoretical and experimental studies for variation of several parameters such as pH, temperature, cross linking, number of cycles, adsorption sites etc. This will be attempted to ensure optimum adsorption performance for metal recovery from waste.

2.2 To Prevent/Minimize Open Air Burning of Rice Straw by Channeling it as a Cellulose Resource

Rice straw does not find use as an animal feed because of its poor nutritional value. Some alternatives for upcycling rice straw are use in paper/pulp and brick kilns industries, but these options are not economically lucrative for farmers.

Due to above mentioned reasons, open air burning practices are prevalent in Indian farms to dispose the huge amounts of rice straw produced. These practices are proven to be a major source of annual GHG emissions of India.

2.3 To Design a Novel Green Process for Synthesis of Hydrogel

This study aims at modifying the reported synthesis routes of cellulose hydrogel production by replacing the chemicals/processes by environment friendly alternatives. For instance, replacing analytical grade alkali with petha waste water and high temperature heating with microwave irradiation or sonication is intended. Plant based crosslinking/gelling agent would also be used.

2.4 To Provide a Greener, Economical, Practical and Scalable Alternative for Conventional Industrial Adsorbents

Major industrial adsorbents in use presently are activated carbon based, which is a carbonaceous material derived from charcoal. Few other conventional industrial adsorbents are activated alumina, zeolites, nanomaterials. Activated carbon is produced by pyrolysis of organic matter followed by activation, which is a highly energy intensive process causing significant amount of GHG emissions. A cellulose-based adsorbent produced via greener synthesis routes is targeted by this study. The process will be designed in such a way so that it is scalable, practical, and cost effective.

3. Literature Review

3.1 Rice Straw as a Cellulose Resource

According to Bhuvaneshwari et al. (2019), 37 million tons of rice straw is burnt yearly in India contributing to major share of agricultural Green House Gas (GHG) emission. Significant number of studies have been reported on feasibility of exploitation of rice straw as cellulose resource with a yield of 29-35 weight %. Cellulose is polymer of cellobiose, which consists of β-D-glucopyranose units linked via β-(1,4) glycosidic bonds. Cellulose chains are arranged together to form micro-fibrils and fibrils, which are embedded in the lignocellulosic matrix (Zoghlami and Paës 2019). It makes up 30.3-38.2 percent of rice straw on dry weight basis (Jin and Chen 2007). Structural features of rice straw include a cell wall of lignin polymer surrounding cellulose and hemicellulose fibers, known as lignocellulosic matrix. This recalcitrant structure needs to be broken down into individual constituents for isolation of cellulose (Chundawat et al. 2011).

The treatment required for this disintegration of lignocellulosic biomass is known as "pretreatment" of lignocellulosic biomass. Pretreatment studies of rice straw with petha waste water have been reported by host institution (Bio-hydrogen Lab at DEI, Agra) with significant increase in cellulose release from lignocellulosic matrix (Kumari and Singh 2020; Kumari et al. 2021; Kumari and Singh 2022)

Post pretreatment, isolation/purification of cellulose is done by removing the hemicellulose and lignin using centrifugation followed by vacuum filtration. Residual amount of hemicellulose and lignin can be removed using reflux, acid wash, hot water wash, bleaching and other similar techniques (Nuruddin et al. 2016; Wirjosentono and others 2017).

3.2 Synthesis of Cellulose Hydrogel

Cellulose Hydrogel synthesis has been reported both by native cellulose and cellulose derivatives. A major challenge in the process is lack of specific solvent for cellulose because extensive amount of hydrogen bonding present in the structure (Kang et al. 2016; Mondal 2019). This extensive hydrogen bonding also gives rise to hydrophobic nature of cellulose. Specific solvent systems such as ionic liquid/organic solution; e.g., LiCl with N-methylmorpholine oxide (NMMO), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), paraformaldehyde (PF) etc. have been reported (Chang and Zhang 2011). Ionic liquids in solvent system minimize the extent of hydrogen bonding (Zhang et al.

2014). Solvent system and dissolution temperature have significant impact on optical and mechanical properties of hydrogel (Kim et al. 2012). Next step after dissolution is physical or chemical cross linking to build a three-dimensional gel network.

3.2.1 Physical Synthesis Methods

The hydrogel obtained by physical synthesis methods consist of non-covalent cross linking, and thus are reversible networks. These non-covalent forces can be Vander Waals forces, hydrogen bonds, hydrophobic or electronic interactions (Shen et al. 2016).

Polymeric cellulose solutions are completely isotropic at low concentration, which signifies the low degree of crystallinity. With increase in concentration, polymer chain entanglement and hydrogen bonding increases and the transitioning from solution (liquid) to crystalline solid is initiated (Song et al. 2011). This mechanism is also known as gelation and it generally takes place at elevated temperatures.

3.2.2 Chemical Synthesis Methods

Chemical synthesis methods produce hydrogels with covalent bond network and is preferred over physical synthesis methods because it results in an irreversible gel network with higher stability, absorbency, superior optical and mechanical properties (Laftah et al. 2011; Hubbe et al. 2013). Plant based cross linking sources are cited by Ul-Islam et al. (2021) (Aloe vera) and Padmanabhan et al. (2022) (Orange peel). Prominent method of achieving chemical cross linking is via homogeneous solution polymerization, where the monomer, initiator, cross linking agent and polymer all are in one phase. This polymerization type proceeds through free radical mechanism (Bao et al. 2011).

An alternative method is inverse phase suspension polymerization where the monomer is generally in dispersed phase and other reagents are dispersed in continuous phase (Liu et al. 2009). One of the lesser known, but emerging technique for chemical cross linking is microwave irradiation. Dipoles of reactants/solvent molecules and microwave radiation interact to produce “dielectric heating”, which is the driving force for the reaction.

3.3 Theoretical Adsorption Studies using Density Functional Theory

Density Functional Theory works on the axiom that electron density of a molecule determines its properties; such as Gibbs energy, enthalpy, Frontier Molecular Orbital (FMO), vibration frequency etc. (Cohen et al. 2012). For study of adsorption, density functional theory finds application in calculating

binding energy for adsorption, preferential adsorption sites, spatial arrangement, natural bond orbital analysis, thermodynamic stability, reactivity indices derived via FMO analysis etc. Few recent DFT studies on metal-adsorbent system are summarized in **table 1** below.

Table 1. Absorption variables studied with Density Functional Theory

System	Variables	Software	Functional	References
Ni^{2+}/Graphene Oxide	Preferential adsorption sites, binding energy	Gaussian 09	PBE1PBE	Chen et al., 2016
Cd^{2+}/Cellulose Biochar	Preferential adsorption sites, binding energy, electron sharing	Materials Studio DMoL3	PBE	Chen et al., 2018
Cd^{2+}, Cu^{2+}, Cr^{2+}/Cellulose and Cellulose acetate	Adsorption mechanism, reactivity indices, FMO, interaction distances	Gaussian 09	M06-2X	Reis et al., 2020
Pb^{2+}, Hg^{2+}, Zn^{2+} / Lignocellulosic Biochar	FMO, binding energy, thermodynamic stability	Gaussian 09	B3LYP	Sellaoui et al., 2019
Pb^{2+}, Hg^{2+} /CMDEAEC and Cellulose Nitrate	FMO, reactivity indices, Gibbs free energy	Gaussian 09	M06-2X	Costa et al., 2021

3.4 Application of Hydrogel in Metal Recovery

Recovery of some transition metals such as Copper, Lead, Silver, Cadmium, Nickel, Chromium Gold and Mercury using hydrogel has been reported in literature in past (Yang et al. 2011; Dharmapriya et al. 2021). A study by Liu et al. (2010) reported selective adsorption of Uranium ion on chitosan/PVA cross-linked hydrogel. Another study by He et al. (2021) reported recovery of rare earth metals Praseodymium and Thulium by using phosphorylated hydrogel. Adsorption capacities of various hydrogel derivatives quoted in few recent studies are summarized in **table 2** below.

Table 2. Adsorption capacity of hydrogel derivatives

Hydrogel Derivatives	Metals	pH	Adsorption Capacity	References
Thiol-ene hydrogel	Au^{3+}	0.5	45.29 mg/g	Frlak et al. 2012
Chitosan/PVA hydrogel	U^{6+}	5.0	156 mg/g	Liu et al. 2010
Phosphorylated Hydrogel	Pr^{3+}, Tm^{3+}	~5.0	2.14, 1.57 mmol/g	He et al. 2021
Cellulose-Chitosan	Cu^{2+}	5.0	169.49 mg/g	Zhao and Mitomo 2008
CMC-ECH	Cu^{2+}, Ni^{2+}, Pb^{2+}	4.6	6.49, 4.06, 5.15 mmol/g	Yang et al. 2011

Chitin	As^{5+}	<6.9	3.1 mg/g	Ramos et al. 2016
Allylthiourea	Ag^{+1}, Pd^{+2}	1	83.33, 152.81 mg/g	Dharmapriya et al. 2021

Data in the **table 2** indicates that hydrogels synthesized from natural sources offer competitive adsorption efficiency with respect to industrial adsorbents, and they have the potential to be a greener alternative for metal recovery.

4. Proposed Methodology

4.1 Materials

4.1.1 Rice Straw

Rice straw will be used as a cellulose resource. It is to be sourced from farms located near host institute, i.e., from Dayalbagh region of Agra.

4.1.2 Petha Waste Water (PWW)

Petha Waste Water will be a pretreatment agent for rice straw in this study. It is to be collected from cottage petha industries located in Noori Darwaja locality of Agra.

4.1.3 Citrus Fruit Peel/Aloe Vera Leaves

Citrus fruit peel as a source of green functional group modifier/cross linking agent, is to be collected from domestic kitchen waste and local fruit juice vendors. Similarly, Aloe Vera leaves is to be collected from gardens/farms in Dayalbagh region of Agra. The study is open to experimentation with other plant-based sources.

4.1.4 Analytical Grade Chemicals

All chemicals used will be acquired from MERCK and Sigma Eldrich.

4.2 Pretreatment of Rice Straw

Pretreatment of Rice straw is to be carried out using highly alkaline petha wastewater having pH 12-14. The pretreatment is intended at separating lignocellulosic biomass into individual components of lignin, cellulose and hemicellulose, and the mechanism of standard pretreatment process is shown in figure 1.1. After size reduction rice straw will be soaked in petha wastewater for one week, after which pH of petha wastewater would decrease to near neutral (Kumari and Singh 2020). The solubilization of lignocellulosic content of rice straw would result in increase in sugar content which will be analyzed

by Dinitrosalicylic acid (DNS) method with respect to glucose as standard. Total carbohydrate content will be analyzed by Anthrone method using UV-Visible spectrophotometer. Compositional analysis of RS for cellulose, hemicellulose and lignin content will be done using acid detergent fiber (ADF), neutral detergent fiber (NDF) and acid detergent lignin (ADL) respectively as described by standard procedures.

4.3 Isolation of Crude Cellulose and Purification

PWW pretreated rice straw will be centrifuged and filtered under vacuum to isolated crude cellulose. After drying, precipitate would be subjected to microwave irradiation, acid wash finally followed by multiple wash cycles with deionized water until neutralized. Additionally, hydrolysis and bleaching will also be carried out to purify the precipitate further. These processes are known to remove residual lignin and hemicellulose (Nuruddin et al. 2016).

4.4 Synthesis of Cellulose Hydrogel

Chemical synthesis by cross linking of cellulose isolated from rice straw will be attempted in this study. Green cross-linking agents (e.g., pectin, citric acid) isolated from plant-based sources will be used. Parameters such as cross-linking temperature, time, pH etc. will be studied for optimization. Processes such as solution polymerization, freeze thaw cycles, microwave irradiation and sonication will be investigated for hydrogel synthesis individually and in combinations.

4.5 Adsorption Studies

4.5.1 Theoretical Studies using DFT

Preferential adsorption sites, binding energy, FMO analysis, thermodynamics of adsorption etc. will be investigated by density functional theory (DFT). The calculations for density functional theory will be done using Gaussian 9, ORCA 5.0.1 and the appropriate molecular structures for the calculation would be created using Gauss view 6 and Avogadro 1.2.0 version.

Major applications of molecular modelling and DFT calculation in present study will be as follows-

- Study of three-dimensional structure and stereo-chemistry, alignment and bond length/distances after adsorption.
- Study of thermodynamics of adsorption by calculation of Gibbs free energy, enthalpy and other thermodynamic quantities.

- FMO analysis with respect to HOMO-LUMO orientation, energy gap, phases etc.

4.5.2 Experimental Studies

Selective metal adsorption will be studied by industry effluent/leached solution of e-waste. Range of concentration can be obtained by dilution for comparative study. Effect of pH, temperature, contact time, effect of initial metal ion concentration will be studied.

Desired amount of adsorbent needs to be added in stock solutions, and the suspensions would be agitated (stirred) for required contact time, pH and temperature for study can be adjusted. Solution needs to be filtered after given amount of time and both filtrate and precipitate will be analyzed using ICP-OES and FTIR spectroscopy. The results of analysis would give important information about change in hydrogel after adsorption, and quantity of metal adsorbed. Metal removal and capacity of adsorption can be calculated following formulas.

$$Metal\ Removal\ (\%) = \frac{(initial\ metal\ conc. - residual\ metal\ conc.)}{initial\ metal\ conc.}\ X\ 100 \qquad (4.1)$$

$$Adsorption\ capacity = \frac{(initial\ metal\ conc. - residual\ metal\ conc.)solution\ volume}{adsorbent\ mass} \qquad (4.2)$$

Mechanism of adsorption can be studied by plotting various adsorption isotherms using experimental data. Experimental set up for column study is proposed to compare the efficiency of batch vs column process (**Fig. 2**). A vertical glass column would be clamped and glass wool, beads or steel mesh can be used to support bio adsorbent. Treated solution would be collected at fixed time intervals and will be analyzed.

4.6 Cost Analysis

Cost analysis will be done using the method mentioned by Gupta et al., (2018). Breakup of total cost for preparing 1 kg of adsorbent from naturally available materials will be calculated by including the cost of biomass, cost of chemicals, cost of energy input used in drying etc. and overhead cost. From efficiency of biosorption, cost of recovery of 1 gm of metal can be calculated and compared with commercial adsorbent such as activated carbon.

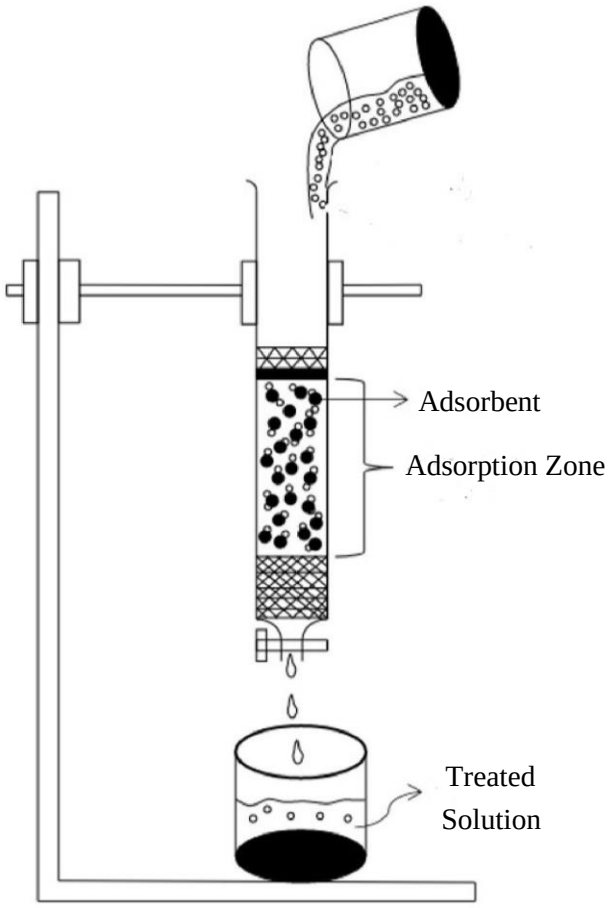

Figure 2. Schematic for column adsorption setup

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